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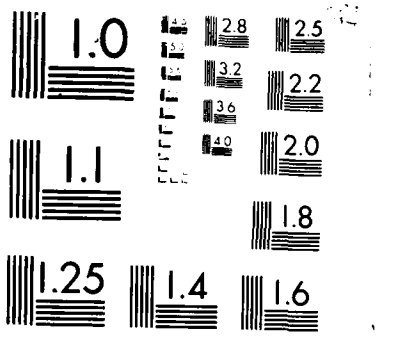

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During the six month period April 1, 1985—September 30, 1985, efforts on the Program "Synthetic Metals from Intercalated Graphite" were largely focused on studies of magnetic graphite intercalation compounds. Experimental studies on the acceptor compounds were directed toward elucidation of the magnetic field–induced phase changes at low fields (less than 500 Oe) of a prototype compound, stage 1 $CoCl_2$–GIC. Theoretical modeling identified the anomalies in the observed magnetic susceptibility with specific magnetic phase transitions, thereby determining the magnitudes of the in–plane symmetry–breaking field and the interplanar magnetic coupling for this model system for 2D–XY magnetic behavior. Theoretical models for finite size effects and competing symmetry–breaking fields were developed to interpret magnetic susceptibility measurements. Studies of magnetic field–induced phase transitions at high magnetic fields were explored in the model donor compound C_6Eu to gain insight into magnetic interactions between the graphite π electrons and intercalant f–electrons. High resolution transmission electron microscopy studies focused on a detailed understanding of the novel electron beam induced phase change in $SbCl_5$–GICs, a computer simulation of the lattice images in the $SbCl_5$–GICs to identify the molecular arrangement in the lattice and finally on a detailed study of the in–plane and c–axis structure of the ternary KH_x–GICs. Studies of the electronic structure were directed toward understanding charge transfer processes in ternary donor GICs and acceptor GICs.

~~Second Semi~~-Annual Report
to the
Air Force Office of Scientific Research
for research on

Synthetic Metals from Intercalated Graphite

AFOSR Contract #F49620-83-C-0011
for the period
April 1, 1985 — September 30, 1985

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1 Overview

This Semi-annual report contains a restatement of the proposed research under AFOSR contract #F49620-83-C-0011 on "Synthetic Metals from Intercalated Graphite" and reports the current state of the work.

1.1 Abstract of Objectives

During the six month period April 1, 1985—September 30, 1985, efforts on the Program "Synthetic Metals from Intercalated Graphite" were largely focused on studies of magnetic graphite intercalation compounds. Experimental studies on the acceptor compounds were directed toward elucidation of the magnetic field-induced phase changes at low fields (less than 500 Oe) of a prototype compound, stage 1 $CoCl_2$-GIC. Theoretical modeling identified the anomalies in the observed magnetic susceptibility with specific magnetic phase transitions, thereby determining the magnitudes of the in-plane symmetry-breaking field and the interplanar magnetic coupling for this model system for 2D-XY magnetic behavior. Theoretical models for finite size effects and competing symmetry-breaking fields were developed to interpret magnetic susceptibility measurements. Studies of magnetic field-induced phase transitions at high magnetic fields were explored in the model donor compound C_6Eu to gain insight into magnetic interactions between the graphite π electrons and intercalant f-electrons. High resolution transmission electron microscopy studies focused on a detailed understanding of the novel electron beam induced phase change in $SbCl_5$-GICs, a computer simulation of the lattice images in the $SbCl_5$-GICs to identify the molecular arrangement in the lattice and finally on a detailed study of the in-plane and c-axis structure of the ternary KH_x-GICs. Studies of the electronic structure were directed toward understanding charge transfer processes in ternary donor GICs and acceptor GICs.

1.2 Statement of Work

Statement of work in AFOSR contract #F49620–83–C–0011 on "Synthetic Metals from Intercalated Graphite".

- Derive techniques for improved methods for the preparation and characterization of specific graphite intercalation compounds.

- Synthesize new intercalated systems and study their structure.

- Study in–plane structure and phase transitions in the intercalate layers with electron diffraction, lattice fringing, real space electron microscope imaging, and high resolution x–ray scattering.

- Deduce structural phase diagrams for specific graphite intercalation compounds.

- Investigate in detail commensurate–incommensurate phase transitions.

- Study lattice modes by infrared and Raman spectroscopy, and inelastic neutron scattering.

- Derive models for the phonon dispersion relations throughout the Brillouin zone, and apply these models to interpret lattice mode studies.

- Model the electronic dispersion relations and apply these models to interpret the experimental results relevant to the electronic properties.

- Measure and model thermal transport phenomena in intercalated graphite.

- Measure the temperature and field dependence of the magnetic susceptibility and heat capacity of magnetic graphite intercalation compounds and to construct magnetic phase diagrams for these systems.

- Study the superconductivity of specific graphite intercalation compounds.

2 Current Status of Research Effort

A summary of the current status of the research effort on "Synthetic Metals from Intercalated Graphite" is presented in the following sections. In presenting the summary, we refer by number (#n) to the publications for the six month period April 1, 1985 to September 30, 1985 listed in Section 3.1.

2.1 Low Dimensional Magnetism in Magnetic Graphite Intercalation Compounds

The $CoCl_2$–GIC system has been selected as a prototype system for the investigation of low dimensional magnetic phenomena because of its exceptionally high magnetic anisotropy. Thus among the various graphite intercalation compounds that have been synthesized, the $CoCl_2$–GIC system is the best candidate for a two–dimensional magnetic system.

During the six months of this reporting period a full length paper was completed on the experimental observation of magnetic field–induced phase transitions in the stage 1 $CoCl_2$–GIC system, and on the interpretation of these experiments. A Monte Carlo calculation of this phenomenon was also initiated. Several theoretical papers on finite size effects and competing field effects were published to provide insight into the interpretation of the experiments. Experimental studies of the magnetoresistance of the stage 1 donor compound C_6Eu were carried out and a preliminary report was completed. Further experimental studies and a Monte Carlo simulation of the phenomena are in progress.

2.1.1 Magnetic Field–Induced Transitions in $CoCl_2$–GICs

Two field–induced susceptibility anomalies have been observed at low temperatures (below the lower critical temperature T_{cl}) in the quasi two–dimensional spin system of $CoCl_2$–intercalated graphite (# 9, # 13). A theoretical model has been developed to explain these anomalies using the Landau free energy functional applied to the magnetic Hamiltonian of $CoCl_2$–intercalated graphite. The interpretation of these experiments yields important information on the magnetic interactions of this system. The low field anomaly at $H_{AS}(T) \approx 160$ Oe is identified with a two–dimensional antiferromagnetic–spin–flop first–order transition. The high field anomaly at $H_{SF}(T) \approx 300$ Oe is identified with a spin–flop–ferromagnetic second–order transition. The low temperature properties of these three phases in the stage 1 $CoCl_2$–GIC are analyzed using the transfer matrix method for their c–axis ordering. A comparison of the theory with experimental susceptibility data indicates that the antiferromagnetic coupling between Co^{2+} layers and the 6–fold in–plane anisotropy field are approximately 160 Oe and 10 Oe, respectively. Since the magnetic islands contain about 4000 spins, the $CoCl_2$ system is particularly well suited to a Monte Carlo calculation of the spin states in the magnetic phase diagram. Such a Monte Carlo calculation has been carried out and has been especially helpful in identifying the spin arrangements in the low temperature magnetically ordered phases. Further refinements in the Monte Carlo calculations are in progress.

2.1.2 Zero Field Susceptibility of Finite Size Kosterlitz–Thouless Systems

Experimentally we find that the magnetic intercalate layers in the $CoCl_2$–GIC system are not homogeneous, continuous layers but rather form island structures. For an infinite 2D–XY system, the magnetic susceptibility diverges at the Kosterlitz–Thouless transition. To interpret our magnetic susceptibility measurements for samples containing finite size magnetic islands, finite size effects on the Kosterlitz–Thouless transition have been investigated using the renormalized spin wave–vortex gas method (# 6). By imposing an upper limit on the length scale and a lower limit for the spin wave integral, the finite size rounding of the susceptibility in the 2D–XY model has been obtained. The differential magnetic susceptibility has been calculated numerically by integrating the spin–spin correlation function and the result has been normalized to the high temperature series expansion for the classical 2D–XY model. Application of this theory has been made to the $CoCl_2$-intercalated graphite system.

2.1.3 Competing Field–Induced Transitions in the Two–Dimensional XY Model

In studying the magnetic properties of $CoCl_2$–GICs, two symmetry breaking fields are present: the in–plane 6–fold crystal field and the external magnetic field. In this connection the ferromagnetic two–dimensional XY model with a p–fold symmetry–breaking field H_p, subjected to an in–plane external field H applied at an angle ω $(0 \leq \omega \leq \pi/p)$ with respect to the p–fold axis, has been analyzed exactly at zero temperature (# 3). A spin–flip type transition occurs at a critical field $H_C = p^2 H_p$ and at a critical angle $\omega_0 = \pi/p$. At this critical point, the parallel differential susceptibility, $\chi_{\parallel}$, (where the probing field $h_{\parallel}$ is parallel to H), jumps discontinuously to zero and the perpendicular differential susceptibility, $\chi_{\perp}$, (where the probing field $h_{\perp}$ is perpendicular to H), diverges like $(H_C - H)^{1/2}$. A self consistent harmonic approximation has been applied for the low temperature analysis, and numerical results for the magnetization, the parallel susceptibility and the perpendicular susceptibility have been obtained. The singularities of the zero temperature analysis are retained when random averages are taken numerically over the angle ω for the parallel susceptibility and magnetization. These concepts have been applied to measurements of the magnetic properties of two–dimensional systems.

A generalization of the José, Kadanoff, Kirkpatrick and Nelson(JKKN) model has been made to multiple symmetry–breaking fields using the classical 2D–XY model (# 2). The calculation applies symmetry arguments to the renormalization group equations. The generalized model has been analyzed using a renormalized spin wave–vortex gas technique, with finite size effects included. Numerical results for the generalized model have been obtained for the case of a classical 2D–XY model with a 1–fold symmetry–breaking field and a 6–fold symmetry–breaking field. Applications of the generalized JKKN model have also been made to the susceptibility measurements on $CoCl_2$–intercalated graphite.

2.1.4 Temperature Dependence of the Magnetic Susceptibility of $CoCl_2$-GICs

Previously measured differential magnetic susceptibility data for stage 1, 2 and 3 $CoCl_2$–GIC samples have been analyzed using the high temperature series expansion of the classical spin model in two dimensions, yielding conclusive evidence for a classical 2D–XY model description of the

magnetic properties of $CoCl_2$–GICs (# 7). Deviations from the high temperature series analysis have been studied using the theory of the finite size Kosterlitz–Thouless transition, with size as an adjustable parameter. The results indicate that the island size in the $CoCl_2$–intercalate layer is of the order of 60×60 to 80×80, consistent with our previous findings using transmission electron microscopy. The effect of the symmetry–breaking field has been analyzed using a generalized JKKN model and a qualitative understanding of the susceptibility anomalies in $CoCl_2$–GICs has been achieved. It is found that the $CoCl_2$–GICs are well described by a classical 2D–XY system with a ferromagnetic exchange coupling $J_{eff} = 7.125\ K$. A Kosterlitz–Thouless transition takes places at $T \approx 10\ K$ and the divergent susceptibility is rounded off by finite size effects as well as the effects of the probing field. The initial decrease in the susceptibility for $T \leq 10\ K$ is a result of the in–plane 6–fold symmetry–breaking field as well as the interplanar coupling; the low temperature phase is consistent with the picture of ferromagnetic layers of XY spins coupled antiferromagnetically.

2.1.5 High Field Magnetoresistance and Magnetic Phase Transitions in C_6Eu

The only donor magnetic GIC that has been prepared in a form suitable for magnetic measurements is the first stage compound C_6Eu. We have studied the magnetic phase diagram for this compound using high field magnetoresistance techniques, employing the highest fields available with the hybrid magnet at the Francis Bitter National Magnet Laboratory.

Specifically, the high field magnetoresistance $\rho(H)$ of the antiferromagnet C_6Eu has been investigated for configurations of $\vec{H} \perp \hat{c}$ and $\vec{H} \parallel \hat{c}$ (# 10). The longitudinal magnetoresistance $\rho_\ell(H_\perp)$ for the $\vec{H} \perp \hat{c}$ orientation shows a drastic decrease at H_{c0}, the metamagnetic transition field, in going from the low field antiferromagnetic (Δ) state to the ferrimagnetic (FI) state; an increase in $\rho_\ell(H_\perp)$ at H_{c1} has also been reported where H_{c1} is the transition field from the ferrimagnetic state to the canted state. The transverse magnetoresistance $\rho_t(H_\perp)$ for $\vec{H} \perp \hat{c}$ shows a kink at H_{c2}, the highest transition field from the canted to ferromagnetic states. The longitudinal magnetoresistance $\rho_\ell(H_\perp)$ also shows an anomaly at H_{c2}. Furthermore, the transverse magnetoresistance $\rho_t(H_\parallel)$ for $\vec{H} \parallel \hat{c}$ shows a clear anomaly at the transition field to the ferromagnetic state, and also other anomalies at lower fields. The magnetic phase diagram implied by the magnetoresistance measurements has yet to be determined. Further measurements are in progress to study the behavior in the canted phase in more detail.

2.1.6 Electrical Resistivity, Magnetoresistance and Magnon Drag Effect in C_6Eu

The localized f–electron spin system in C_6Eu exhibits four different spin configurations with varying magnetic field applied in the basal plane, and the in–plane resistivity shows interesting magnetic field and temperature–dependences associated with each spin configuration (# 12). To interpret these experimental results, the electrical resistivity and magnetoresistance have been calculated taking into account the spin fluctuation scattering due to the π–f exchange interaction. The deviation of the magnon distribution from thermal equilibrium plays an important role in the temperature dependence of the magnetoresistance.

2.2 High Resolution Electron Microscopy Studies of Graphite Intercalation Compounds

During this six month period, several different high resolution structural studies have been completed. In one study, the highly novel electron beam damaged–induced structural phase change in $SbCl_5$–GICs has been investigated in detail, to gain a better understanding of the phenomenon and its underlying mechanism. To achieve insight into the possible molecular arrangements of an intercalant which disproportionates upon intercalation, a computer image simulation was carried out and compared with the measured lattice fringe images. In addition, high resolution transmission electron microscopy studies of the ternary KH_x–GICs were carried out to help interpret our studies of the structure/property relations of these ternary compounds.

2.2.1 Electron beam induced damage and structure of $SbCl_5$ graphite intercalation compounds

Detailed high resolution transmission electron microscopy studies (# 17) show that the commensurate–solid to glass phase change previously reported in $SbCl_5$–intercalated graphite is attributed to electron beam damage in the transmission electron microscope. The damage process has been studied as a function of electron dose and energy. Two competing annealing processes have been identified, each with a different activation energy. High resolution lattice images obtained with electron doses below the damage threshold are compared with simulated images based on a variety of structural models for the intercalate. The coexistence of two molecular species in the commensurate phase is necessary to fit the high resolution images and to explain the mechanism for damage. The electron beam–induced damage process provides a controlled means of producing a quasi–two dimensional glass phase.

2.2.2 Image Simulation of the Molecular Arrangement in the $SbCl_5$–GIC System

High resolution lattice images of $SbCl_5$–GIC samples were taken at room temperature under axial illumination by placing an objective aperture that encompassed reflections up to the (100) ($q = 1.108$ Å^{-1}) $(\sqrt{7} \times \sqrt{7})R19.1°$ superlattice reflections for the in–plane images, and the (004) ($q = 1.971$ Å^{-1}) reflection for the c–axis lattice images (# 17). Images from the same sample region were obtained under different focus conditions. The lattice images were obtained by finding approximately the in–focus condition and then taking an under focus series of pictures in steps of -280 Å. The interplanar spacings were obtained from optical diffractograms taken from the negatives of the lattice images. More accurate values for the defocus conditions were estimated from optical diffractograms taken from the disordered background contained in some areas of the negatives of the TEM micrographs. A multi–slice calculation was carried out to simulate the observed lattice images in order to identify the structural arrangement of the molecular species.

Good agreement was obtained between the experimental TEM and simulated images of the (00ℓ) planes for $SbCl_6^-$ and $SbCl_3$ in a specific stacking sequence and for $SbCl_6^-$ and $SbCl_5$ in another stacking sequence. Based on the results for the in–plane and c–axis simulated images, we consider the $(\sqrt{7} \times \sqrt{7})R19.1°$ regions more likely to be formed by a mixture of either $SbCl_6^-$ and $SbCl_3$ molecules with no Sb^{5+} to Sb^{3+} long range order, or by $SbCl_6^-$ and $SbCl_5$ molecules containing

only the Sb^{5+} species. One advantage of the model of a mixture of $SbCl_6^-$ and $SbCl_3$ molecular species in the $(\sqrt{7} \times \sqrt{7})R19.1°$ phase is that it can be used to explain the radiolysis process and the annealing mechanisms of electron beam induced damage effects described above (# 17).

2.2.3 High Resolution Transmission Electron Microscopy on KH_x–Graphite Intercalation Compounds

The in–plane and c–axis structure of KH_x–GICs was studied using high resolution transmission electron microscopy (TEM) and x–ray diffraction as a function of intercalation temperature and time (# 16). With TEM, two commensurate in–plane phases were found to coexist in these compounds with relative concentrations depending on intercalation conditions. When the direct intercalation method was used, the first step in intercalation was the formation of a stage n potassium–GIC and the final compound was a stage n KH_x–(KH_y)–GIC. High resolution (00ℓ) lattice images show direct evidence for intermediate phases in the intercalation process. These intermediate phases are hydrogen (deuterium) deficient and are found at the boundary between pure potassium regions and regions with high hydrogen (deuterium) content. Since electron beam–induced desorption of hydrogen takes place during the TEM observations, information has been obtained about the structural effects of hydrogen desorption (# 16).

2.3 Electronic Properties

Our studies of the electronic properties during this six month reporting period focused on the fundamental differences in the charge transfer mechanism in donor and acceptor graphite intercalation compounds. For the case of the acceptor compounds we have reviewed the previously proposed mechanism for the charge transfer, and propose a new approach to treating the charge transfer. For the donor compounds we have examined (using the Shubnikov–de Haas Effect) the competition of the graphite layers with another acceptor–type (hydrogen) layer for the electrons transferred from a donor (potassium) layer in a compound where the charge transfer can be described by an overlapping band model.

2.3.1 Charge Transfer Mechanism in Acceptor–GICs

Despite the fractional charge transfer in acceptor GICs, the density of states for these compounds can not be treated by an overlapping band model as is characteristic of donor GICs. There are thus fundamental differences between the charge transfer mechanism in acceptor and donor compounds. Instead of an overlapping band model, a variety of other charge transfer mechanisms have been proposed for acceptor GICs. Previously proposed disproportionation and islandic models for charge transfer have been critically reviewed (# 8). To treat commensurate intercalants with a filling factor of unity, a mechanism for acceptor charge transfer based on band effects is proposed. Such a mechanism may be valid for molecular acceptor compounds (such as Br_2–GICs) which exhibit a commensurate intercalate layer with long range in–plane coherence. For acceptor compounds such as the Br_2–GICs, defect mechanisms such as disproportionation and intercalate island structures cannot account for charge transfer.

2.3.2 Shubnikov–de Haas Experiments on Potassium–Hydrogen Graphite Intercalation Compounds KH_x–GICs

Potassium–hydrogen–graphite ternary compounds KH_x–GICs ($0 < x < 1$) are donor type compounds containing an ionic intercalant K^+H^-. Basically the effect of hydrogen addition is the uptake of electrons from the potassium so that fewer electrons are available for conduction in the graphitic π–bands. To obtain Fermi surface information directly, Shubnikov–de Haas (SdH) measurements were carried out on stage–1, 2 and 4 KH_x–GICs. The results are compared with the electronic properties of K–GICs and KHg_x–GICs. The observed Shubnikov–de Haas oscillations are qualitatively modeled using the three dimensional dilute–limit model. These Fermi surface results are related to other experiments on KH_x–GICs, such as magnetic susceptibility, electronic specific heat, Raman scattering and superconductivity. For example, it is found that because of the strong electron affinity of hydrogen, the charge transfer to hydrogen and graphite in stage–2 KH_x–GICs completely depletes the electrons in the potassium conduction band, consistent with the experimental specific heat results. The basic conclusion that the uptake of hydrogen results in a lower electron concentration in the graphite π–bands is supported by all experiments.

Results on the Fermi surface for KH–GICs have been obtained using the Shubnikov–de Haas effect (# 18). Characteristic Shubnikov–de Haas frequencies have been observed for stage 1, 2 and 4 KH–GICs. Each of the spectra have been analyzed in terms of the rigid band model, but it is only for stage 4 that good agreement is obtained with the model, as would be expected since stage 1 and stage 2 should not be well described by the dilute limit model. The interpretation of the Shubnikov–de Haas results assumes full occupation of the hydrogen levels, consistent with the strong electron affinity of hydrogen.

2.4 Implantation–Enhanced Intercalation

We have shown that if a graphite sample is first ion implanted, then the ability to intercalate certain species is greatly enhanced. This concept has been applied to enhance the intercalation of sodium, which does not readily intercalate graphite. Since the implantation of carbon and argon into graphite also enhances the subsequent intercalation of sodium, we conclude that implantation–enhanced intercalation is due to a defect mechanism rather than to a catalytic process. The extension of the implantation–enhanced intercalation concept to other intercalants has had limited success. This study was the topic of an M.S. thesis completed by H. Menjo in May 1985.

2.5 Model for Staging in Intercalated Graphite

A model for staging has been developed (# 4) based on an evaluation of the partition function for attractive in–plane and repulsive interplanar interactions. The model is carried out analytically and agrees with the numerical calculation of Safran in the limit of Coulomb interactions. Mixed staging is found at high temperatures below the disordering temperature. This study is being carried out in collaboration with Professor David Adler and his graduate student J.C. Schön.

2.6 Thermal Expansion Coefficient of Graphite Intercalation Compounds

Graphite has essentially a zero in–plane thermal expansion coefficient, and a very large c–axis expansion coefficient. For compounds where the intercalant is commensurate with the graphite layers, the in–plane thermal expansion of the intercalant is restricted to very small values. No such constraint applies to the c–axis thermal expansion. To compare the c–axis thermal expansion in a commensurate GIC to that of graphite, the c–axis thermal expansion coefficient of $SbCl_5$–GICs has been obtained from analysis of (00ℓ) x–ray diffractograms for stages 1–3. The contributions to the thermal expansion coefficient of each type of layer along the c–axis has also been obtained, and shown to be very different from one another. A decrease in thermal expansion coefficient with increasing stage is observed and this is related to a higher charge transfer for the higher stages than for the lower ones.

2.7 High Magnetic Field–Induced Charge Density Wave Phase in Graphite

Our investigation of the magnetic field induced charge density wave phase in graphite has recently focused on non–ohmic transport phenomena associated with this phase transition (# 14), and these phenomena are observed at electric fields on the order of 100 mV/cm. The non–ohmic behavior shows a strong dependence on both temperature and magnetic field. The phenomena cannot be explained on the basis of a simple picture of an electric field–induced depinning of the CDW.

2.8 Review Articles and Plenary Invited Talks

During this six month period, several review papers were completed. A tutorial article on "Intercalation Compounds" for a general readership was published in the *Materials Research Encyclopedia* (# 1). A written version of an invited (plenary) paper to the European Physical Society on "Layered Crystals and Intercalated Compounds" was published (# 4). In her retiring Presidential Address, M.S. Dresselhaus spoke about her perspectives on the Presidency of the American Physical Society (# 5), quoting from research work on graphite intercalation compounds supported by this contract. In a plenary (opening) talk at the Fourth International Conference on Intercalated Graphite at Tsukuba, Japan (1985),an overview of the "Opportunities and Challenges in Graphite Intercalation Compounds" was presented and a review article on this topic has been prepared.(# 11)

3 Reports and Publications

3.1 Publications

1. **"Intercalation Compounds"**, M.S. Dresselhaus, *Encyclopedia of Materials Science and Engineering*, edited by Michael B. Bever, Pergamon Press, England (1986).

2. **"Two–Dimensional XY Model with Multiple Symmetry–Breaking Fields"**, K.Y. Szeto and G. Dresselhaus, *Phys. Rev. B* 32, 3142 (1985).

3. **"Competing Field Induced Transitions in the Two–Dimensional XY Model"**, K.Y. Szeto and G. Dresselhaus, *J. Phys. C*, (in press) (1986).

4. **"Layered Crystals and Intercalated Compounds"**, M.S. Dresselhaus, *Advances in Solid State Physics* **XXV**, 21 (1985).

5. **"Perspectives on the Presidency of the American Physical Society"**, M.S. Dresselhaus, *Physics Today*, July 1985, p. 37.

6. **"Zero Field Susceptibility of Finite Size Kosterlitz-Thouless Systems"**, K.Y. Szeto and G. Dresselhaus, *Phys. Rev.* B32, 3186 (1985).

7. **"Temperature Dependence of the Magnetic Susceptibility of $CoCl_2$–GICs"**, K.Y. Szeto, S.T. Chen and G. Dresselhaus, *Phys. Rev.* B32, 4628 (1985).

8. **"Charge Transfer Mechanism in Acceptor-GICs"**, M.S. Dresselhaus and G. Dresselhaus, *Synth. Metals* 12, 79 (1985).

9. **"Magnetic Phase Transitions in $CoCl_2$-Graphite Intercalation Compounds"**, G. Dresselhaus, S.T. Chen and K.Y. Szeto, *Synth. Metals* 12, 433 (1985).

10. **"Magnetoresistance and Magnetic Phase Transitions in C_6Eu"**, H. Suematsu, H. Minemoto, K. Ohmatsu, Y. Yosida, S.T. Chen, G. Dresselhaus and M.S. Dresselhaus, *Synth. Metals* 12, 377 (1985).

11. **"Opportunities and Challenges in Graphite Intercalation Compounds"**, M.S. Dresselhaus, *Synth. Metals* 12, 5 (1985).

12. **"Theory of Electrical Resistivity, Magnetoresistance and Magnon Drag Effect in Graphite Intercalation Compound C_6Eu"**, K. Sugihara, T.S. Chen and G. Dresselhaus, *Synthetic Metals* 12, 383 (1985).

13. **"Two–Dimensional Spin–Flop Transition in $CoCl_2$–Graphite Intercalation Compounds"**, K.Y. Szeto, S.T. Chen and G. Dresselhaus, *Phys. Rev.* B33, 3453 (1986).

14. **"Non–Ohmic Transport in the Magnetic–Field–Induced Charge Density Wave Phase of Graphite"**, Y. Iye and G. Dresselhaus, *Proceedings of the 2D Conference in Kyoto*, 1985.

15. **"Thermal Expansion Coefficient of $SbCl_5$–GICs"**, L. Salamanca–Riba and M.S. Dresselhaus, *Carbon*, (in press) (1986).

16. **"High Resolution Transmission Electron Microscopy on KH_z–GICs"**, L. Salamanca–Riba, N.C. Yeh, M.S. Dresselhaus, M. Endo and T. Enoki, *J. of Mat. Res.* (in press) (1986).

17. **"Electron Beam Induced Damage and Structure of $SbCl_5$ Graphite Intercalation Compounds"**, L. Salamanca-Riba, G. Roth, J.M. Gibson, A.R. Kortan, G. Dresselhaus and R.J. Birgeneau, *Phys. Rev.* B33, 2738 (1986).

18. **"Shubnikov-de Haas Experiments on Potassium-Hydrogen Graphite Intercalation Compounds KH_x-GICs"**, T. Enoki, N.C. Yeh, S.T. Chen and M.S. Dresselhaus, *Phys. Rev.* B33, 1292 (1986).

3.2 Advanced Degrees and Honors

- L. Salamanca-Riba, Ph.D., Physics, July, 1985
  "Structural Studies of Graphite Intercalation Compounds and Ion Implanted Graphite"

- H. Menjo, M.S., Department of Materials Science and Engineering, June, 1985
  "Enhanced Intercalation of Graphite by Ion Implantation"

- M.P. Kudisch, B.S., EECS, June, 1985
  "Crystal Growth and Properties of Graphite Intercalation Compounds"

- M.S. Dresselhaus
  elected to National Academy of Science, April, 1985.

- M.S. Dresselhaus
  appointed Chancellor's Visiting Professor, University of California, Berkeley, Spring, 1985.

4 Personnel Involved with Research Program

- Mildred S. Dresselhaus - Principal Investigator
  Responsible for the research and the direction of all aspects of the program. The study of intercalated graphite is the major research activity in the research group.

- Gene Dresselhaus - Co-Principal Investigator
  Responsible together with the principal investigator for the research and the direction of all aspects of the program.

- Gerhard Roth - Postdoctoral Fellow
  Responsible for high resolution x-ray measurements and for the synthesis and measurements of superconducting properties of graphite intercalation compounds. (Left June 1985 to take an R & D position at Bruker Industries, Karlsruhe, West Germany).

- Ko Sugihara – Research Staff
  Responsible for modeling transport properties of GICs and of scattering processes in magnetic intercalation compounds.

- Alla Antonious – Research Assistant
  Responsible for setting up system for infrared spectroscopy studies in graphite intercalation compounds.

- Alison Chaiken – Research Assistant and Graduate Fellowship Student
  Responsible for superconductivity studies in intercalated graphite, including setting up a ^{3}He refrigeration system.

- Shyng–Tsong Chen – Research Assistant and Graduate Fellowship Student
  Responsible for the synthesis of magnetic intercalation compounds, for high precision measurements of the magnetic susceptibility and magnetization of these compounds as a function of temperature and external magnetic fields. Is also responsible for modeling spin ordering using Monte Carlo techniques.

- H. Jiménez–González, Fellowship Student
  Assigned to exploratory work to determine whether oleophilic graphite flakes can be used to synthesize magnetic graphite intercalation compounds that are difficult to intercalate into HOPG or kish graphite host materials.

- Ali Kazeroonian – Research Assistant
  Responsible for high resolution x–ray measurements of the structure of graphite intercalation compounds, with special emphasis on the possible connection of the in–plane structure to the stabilization of the superconducting transition.

- Hiroshi Menjo – Fellowship Student
  Responsible for synthesis and measurement of the Na-GICs using ion implantation to enhance the intercalation process. Completed M.S. Thesis in May, 1985.

- James Nicholls – Research Assistant
  New student responsible for the synthesis of magnetic graphite compounds, for susceptibility and magnetization measurements, and modeling of two–dimensional magnetic systems.

- Lourdes Salamanca–Riba – Research Assistant
  Responsible for structural studies of intercalated graphite using x–ray diffraction, real space imaging and lattice fringing, with particular emphasis on phase transitions. Completed Ph.D. Thesis in July, 1985.

- Nai–Chang Yeh – Research Assistant
  Responsible for the synthesis, characterization of KHg and KH_x graphite intercalation compounds, and measurement of the Fermi surface, transport properties and magnetic susceptibility.

- Maria Kudisch – Undergraduate Student
  Has been assisting with synthesis of KHg-GICs and superconductivity measurements. Completed B.S. Thesis in May, 1985.

4.1 MIT and Other Collaborators

- D. Adler – Professor, Electrical Engineering, MIT
  Collaborates on models for the intercalation mechanism for graphite intercalation compounds.
- S. Berko – Professor, Physics, Brandeis University
  Collaborates on positron annihilation studies of intercalated graphite.
- R.J. Birgeneau – Professor, Physics, MIT
  Collaborates on high resolution x–ray scattering experiments.
- W. Cooke – Research Staff, Los Alamos Scientific Laboratory
  Collaborates on μ spin rotation studies of $CoCl_2$ intercalated graphite.
- P.C. Eklund – Associate Professor, Physics, University of Kentucky
  Collaborates on lattice mode studies of intercalated graphite.
- J. Murray Gibson – Research Staff, AT & T Bell Laboratories, Murray Hill, NJ
  Collaborates on high resolution microscopy studies of intercalated graphite.
- L. Hobbs – Associate Professor, Materials Science and Engineering, MIT
  Provides expertise in the electron microscopy measurements.
- Y. Iye – Research Staff, IBM Research Labs., Yorktown Heights, NY
  Collaboration on studies of high magnetic field anomaly in graphite.
- P.A. Lee – Professor, Physics, MIT
  Provides expertise on theory of two–dimensional magnetism and high magnetic field anomaly in graphite.
- P.M. Tedrow – Staff Member, Francis Bitter National Magnet Laboratory
  Provides expertise in superconductivity and equipment for carrying out measurements in the millikelvin range.

4.2 Coupling Activities – Seminars and Invited Conference Papers

The MIT group is strongly coupled to international activities on graphite intercalation compounds. Below are listed titles of seminars, invited talks and symposia given over the six month April 1, 1985 to September 30, 1985 period.

- April 12, IBM Research Laboratory, San Jose CA, Laboratory Seminar, "Two–Dimensional Magnetism In Graphite Intercalation Compounds", (MSD).

- April 25, AFOSR, Bolling Air Force Base, Washington, DC, "Opportunities and New Directions In Graphite Intercalation Compounds", (MSD).
- May 17, Xerox Research Laboratory, Palo Alto, CA, Laboratory Seminar, "Two–Dimensional Magnetism In Graphite Intercalation Compounds", (GD).
- May 18, 1985, University of California, Berkeley, CA, School of Engineering, Commencement Address, " The Challenge of Youth", (MSD).
- June 19, 1985, Invited talk, CRDC Scientific Conference on Obscuration and Aerosol Research, June 17–21, 1985, Aberdeen Proving Grounds, MD, "Intercalated Fibers Derived from Benzene", (MSD).
- June 26, General Motors Research Laboratory, Warren MI, Physics Colloquium, "Two–Dimensional Magnetism In Graphite Intercalation Compounds", (GD).
- September 10, General Motors Research Laboratory, Warren MI, Physics Colloquium, "Liquid Carbon", (MSD).

5 New Discoveries, Patents or Inventions

None.

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